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AND
CEMENT MANUFACTURE

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Portland Cement Specifications.

SUGGESTED LOW-GRADE CEMENT.

THE following is an abstract of a paper read by Mr. Alan Moncrieff, M.A., A.M.Inst.C.E., at a recent meeting of the Institution of Structural Engineers.

Modern requirements appear to demand three specifications for Portland cement. No doubt there will be some who disagree with this, but the intention is to examine and discuss the proposition entirely from a user's point of view. It is proposed to term these three grades of cement: 1-Star Standard, 2-Star Standard, and 3-Star Standard. One-star standard would represent a grade somewhat lower than the present standard product so far as fineness and tensile tests are concerned; two-star standard represents the average ordinary standard cement; and three-star standard should represent rapid hardening cements.

First it is necessary to examine the position of average standard cement (two-star). Nearly all manufacturers are producing a cement considerably in excess of the B.S.S. requirements. The fineness test of the B.S.S. allows a 10 per cent. residue on the 170² sieve, but test certificates regularly show that cement is ground to a 5 per cent. or lower residue. The divergence from the requirements of the tensile test may be shown as follows:

	B.S.S. lb. per sq. in.	Actual tests, lb. per sq. in.
Neat cement 7 days (optional) ..	600	800–1,100
Cement-sand 3 days	300	430– 550
7 days	375	530– 650

With these figures before us there would seem no reason why the B.S.S. should not be revised to approximate more nearly to actual conditions.

The position with regard to a standard specification for rapid hardening (3-star) cement must be considered. The latest specification, while acknowledging the need for a standard specification for rapid hardening cement, includes the following paragraph in the foreword: "The Technical Committee has had under consideration the question of including rapid hardening cement in this

revision of the specification, but is of opinion that further research work will have to be carried out in order to be able to say exactly what tests are required to ensure a satisfactory rapid hardening cement, and the Building Research Station is including this material in their investigation. Meanwhile, it may be said that rapid hardening Portland cement is a Portland cement and should comply with this specification." Not a very helpful conclusion after eight years' (1923–31) use of the product. Meanwhile, modern rapid hardening cements exceed the requirements of the B.S.S. of 1931 to such a degree as to make the latter look quite out of proportion.

Tensile tests.	B.S.S. lb. per sq. in.	Actual tests. lb. per sq. in.
Neat cement 7 days (optional) ..	600	850–1,125
Cement-sand 3 days	300	550– 785
7 days	375	650– 840

Fineness tests regularly give a residue of less than 1 per cent. on 170² sieve instead of 10 per cent. as required by the B.S.S. Undoubtedly, the early publication of a B.S.S. for rapid hardening cement would be of great assistance to the cement user.

Further, there would appear to be a demand for a cement of lower grade than the present ordinary standard Portland cement, referred to here as one-star cement. Apart from the question of price, there undoubtedly exists a demand for a standard for Portland cement which is not so finely ground either as the ordinary or rapid hardening grades, and high strengths, whether early or ultimate, are not required in vast quantities of concrete used to-day. Other properties, such as non-porosity and low temperature rise, are often of greater importance than strength, particularly in mass work. It is suggested that a cement complying with, but not considerably exceeding, the present B.S.S. or possibly slightly less stringent requirements in the way of fineness and tensile strength, would fill a great need.

There may be difficulties in this, as the higher strength that is obtained in ordinary and rapid-hardening cements is in some degree a result of striving after other qualities. Hard burning and fine grinding tend to soundness, but they would seem to produce also high temperature rises in setting, which is disadvantageous in works where contraction is a serious problem. Rapid-hardening cement also requires greater care in mixing than one not so finely ground. In fact, each grade has its particular advantages and disadvantages, and it must not be concluded that the proposed one-star grade cement would necessarily be of inferior quality.

On the other hand, it would seem reasonable to expect that one-star cement should be cheaper than ordinary cement. If the present extra price for rapid-hardening cement is due to the harder burning and finer grinding required, then less hard burning and coarser grinding required to produce the one-star grade should cheapen the product. It seems reasonable to assume that as cement, ground to less than 1 per cent. residue on 170² mesh costs about 16 per cent.

more than ordinary cement ground to 5 per cent. residue on 170² mesh, then one-star cement, ground to only 10 per cent. residue on 170² mesh, might be, say, 10 per cent. or more cheaper than ordinary cement. Moreover, there could be a further 2½ per cent. cheapening by using jute sacks (returnable) for packing this grade of cement, instead of paper bags, making a possible saving of, say, 12½ per cent.

The effect of this would be to make it possible to use more one-star cement in what are often harsh lean mixes where ordinary cement is at present used, and with the consequent lowering of the water-cement-ratio to obtain the same degree of workability, the ultimate strength of the concrete might even be greater with one-star cement than were ordinary cement used. Also, the richer one-star cement concrete would certainly be denser and more waterproof. Whether the production of this lower priced cement could be obtained by less burning and coarser grinding, or whether the addition of pozzolana or adulterants would produce the necessary results, it is not proposed to discuss here.

There have been many instances where engineers have considered it advisable to make additions to the cement in the form of pozzolana, or crushed burnt bricks, in some cases for chemical reasons such as the absorption of free lime, and in other cases simply to eke out the cement and yet procure a workable concrete. It therefore may be of interest to record one recent illustration which came to the writer's notice. In 1928, when the construction of the Metur Dam across the Cauvery river in S. India was commencing, it was intended to add 20 per cent. surki to the cement. This surki, consisting of local burnt bricks, was crushed to the following specification: Not more than 3 per cent. to be retained on 50² mesh and at least 66 per cent. to pass the 100² mesh. The proportions of the concrete for the core of the dam were to be 1 : 4 : 8, the cement consisting of 0.8 part cement and 0.2 part surki, and the water-cement-ratio was 8 gallons per bag (1 cwt.). How far these specifications have been followed through the construction has not yet been published. The contention made earlier that vast quantities of concrete are not highly stressed is borne out by the fact that it is believed that no concrete in this work will be stressed beyond 155 lb. per sq. in., whereas test specimens of this lean concrete gave results varying from 933 to 1,244 lb. per sq. in. in compression.

If three standards are ultimately adopted for cement, it would be both desirable and advantageous that each grade should be packed in a different and non-interchangeable packing, and it is suggested that one-star cement be packed in jute sacks (returnable), ordinary cement in paper bags (non-returnable), and rapid-hardening cement in superior paper bags with waterproof linings, or in steel drums. Such differentiation in packings would prevent confusion and reduce the risks of tampering.

In making comparisons of specifications and tests results in these notes it has been necessary to use tensile tests, but with the pending revision of the B.S.S. it is hoped that these tensile tests will be superseded by either compression or beam tests. These latter will be welcomed by the cement user as giving a

better indication of the concrete he may expect. The habit of specifying cement by volume, even at 90 lb. per cu. ft., was wrong and unnecessary. The importance of measuring by weight could not be over-stressed.

There was immediate need for a tentative specification for rapid-hardening cement providing that the fineness residue should not exceed 1 per cent. on 170^2 mesh, and specifying tensile tests at 1, 3, 5 and 7 days. Temperature rise due to setting might be beneficial as well as detrimental. More investigation was needed into the effect of fine grinding upon contraction due to setting as well as contraction due to heat evolution. It was stated that the French authorities were proposing a comprehensive specification for hydraulic cements in nine different groups and thirty-six different grades. Also, American engineers seemed to be expressing dissatisfaction with only one standard specification. Possibly, therefore, it might be thought that his own suggestion, that there should be three specifications, was too conservative.

Discussion.

Mr. W. H. Woodcock said the table in the paper showed that the figure for fineness in the 1931 Specification was 10 per cent. residue on 170^2, whereas in the 1925 Specification the figure was 10 per cent. on 180^2. That might appear to represent a retrograde movement, but actually it represented an advance because the 170^2 sieve had a smaller aperture than the 180^2 sieve. If one regarded a specification as being necessary to force the makers to supply cement giving a high strength at periods of 3 or 7 days there was no reason why we should not increase the specified strength to the figures usually obtained. If, however, the object of the specification was to provide a guarantee that the cement which conformed to it was of good quality and suitable for all ordinary work, then the existing specification covered that point although from time to time the minimum figures could be increased. Sometimes a cement gave figures just a little below the usual figures, and one might then have to reject a good cement because its strength at 3 days was a little below that demanded. There was also the important question whether cement giving a high strength at 3 days was necessarily better than a slower hardening cement which went on hardening over a longer period.

The lecturer had indicated the strength of rapid-hardening cement at 3 and at 7 days, but what was the use of a rapid-hardening cement test at 3 and 7 days if one had not a shorter period test? A short-period test must be introduced, and the suggested period was 24 hours. But a 24-hours' test would give rise to a different problem. There was a latitude of from 30 minutes to nearly 10 hours allowed in the initial set, and a cement which set in 10 hours could not be expected to achieve the same hardness in the remaining 14 hours as would be achieved by a cement which had set within, say, three-quarters of an hour, and had 23¼ hours to harden. In comparatively long periods of 3 and 7 days, a quick start was not of such vital importance, but in a short-period test of 24 hours with rapid-hardening cements, if the hardening properties did not start developing

immediately there would be big variations—and that was exactly what had happened with regard to the 24-hours' test ; we had no method at present which would give reliable results in 24 hours, and that was one of the factors which made it difficult to evolve the specification for rapid-hardening cements.

With regard to the proposed one-star cement for dams, one could wish that the problem of non-porosity and low temperature were as simple as the lecturer seemed to suggest. Fine grinding and high burning could easily be overcome, but there were very many other factors. The question of composition entered into the matter very largely. The amount of heat liberated in the concrete depended on the number of calories liberated and dissipated, and not necessarily on the speed at which they were liberated. If a few calories were liberated rapidly through fine grinding, there was a temporary rise of temperature, which might be greater than that which occurred when there was slow liberation due to coarse grinding provided the heat could be dissipated fairly quickly. But if the heat could only be dissipated very slowly, then the total number of calories came into account, and the effect depended almost entirely on the amount of heat liberated in the reaction between the water and the lime constituents in the cement. In big structures it was more important to use a cement, such as a " low-lime " cement, which would liberate a small number of calories rather than one which would liberate a larger number of calories slowly such as a coarsely ground " high-lime " cement.

Porosity was a problem which was being studied. Even with the most careful grading of aggregates to reduce porosity, in mass work there was always the possibility of porous places, and in order to reduce the bad effects of this the quantity of easily soluble constituents in the set cement should be as low as possible ; for this reason a cement containing a lower percentage of lime (within the usual limits) was preferable to one containing a higher proportion of lime, assuming, of course, that both cements were properly made.

As to the hope expressed that, with the pending revision of the B.S.S., the tensile tests would be largely, if not entirely, superseded by either compression or beam tests, at first sight everyone would agree ; but investigations were being made on this matter with rather surprising results. It had been found that the beam tests had not given such good results as might be expected ; also, in a large series of experiments the mortar cubes had not borne the relation to the concrete cubes that one would expect, and the tensile tests, whilst not satisfactory, had proved as well as any other tests. The question of compression tests on mortar was still being investigated, for it seemed reasonable to expect that, provided the right conditions were found, there should be some relation between the crushing strengths of mortar and concrete. Until these conditions were found, the simple tensile test afforded one of the best indications of the strength developing qualities of the cement, unless one was prepared to carry out much more difficult, and sometimes more erratic, tests on the concrete.

Mr. R. H. Harry Stanger, A.M.Inst.C.E., A.M.I.Mech.E., said this country still retained the tensile test. Every other country, with the exception of

America, used a compression test and relied more on the compression than on the tensile test. A committee of the British Standards Institution had put in hand a series of tests, from which they hoped to find that the mortar compression test agreed fairly well with the concrete compression test. The Building Research Station had discovered the percentage of water which had to be used in the mortar tests to get invariable agreement with concrete results, so that he believed there was a good chance of ousting the tensile test and substituting a test which would be of use and would tell the users of concrete what the material was likely to stand in the course of time.

Mr. T. J. Gueritte said he was aware of the inadequacy, uncertainty and difficulty of tensile tests. But when considering the relative improvement in tensile and compressive stresses recorded during the last fifteen years, one could not fail to be struck by the fact that the improvement had been decidedly slower for tension than for compression. At 90 days the strength in tension used to be 10 per cent. of that in compression; to-day it is found, from a considerable number of tests, that tension was hardly one-thirteenth of compression. In other words, improvement in compression was accompanied by a decrease in ductility and an increase in brittleness, which had some disadvantages. It might be that the striving after high compression tests to the detriment of ductility would receive a fresh impetus if tensile tests were definitely abandoned. If they had to be, then they should be replaced by other tests which would oblige cement makers to improve proportionately tension and compression strength. He was well aware of the advantages of high compression, but equal attention should be given to improvement in tension results.

Mr. D. B. Butler, A.M.Inst.C.E., said it was not only fine grinding that made cement rapid-hardening; in order to make rapid-hardening cement it was necessary to modify the proportions of materials. Again, it was harder burned and finer ground. Most big users had their own specifications for rapid-hardening cement in default of a standard, and the specifications varied considerably. For a long time he had been of the opinion that in the case of very finely ground cement the chief factor was its initial strength, or the strength achieved within, say, a few months. Concrete made with more coarsely ground cement would in two or three years attain as much strength as a concrete made with very finely ground cement. The earlier attainment of the strength in the case of the more finely ground cement was due to the reaction occurring earlier.

Mr. H. R. Cox said manufacturers were bound to be cautious of departing from the standard product. They had to satisfy the customer's demands. They could not put into production ideas for a change until much research had been done, of which nothing was heard unless it produced successful results. The ordinary user did not hear of what manufacturers were doing in the way of research, unless that research was successful. Even though, for some special purposes, variation of the standard cement might be worthy of consideration, the variation must not bring new troubles with it. When responsible makers offered a special cement one could feel assured that it was produced only after

careful research, and was not put on the market hurriedly to meet what was possibly a mistaken theory.

He hoped the lecturer would reconsider his dictum that tensile and fineness tests were more important to the user than chemical composition, soundness, and setting time. Fineness, in its essence, was a means to an end, and he was not even sure that it needed a place in the standard specification at all. The tensile test was only one means of ascertaining strength, and there were others. Chemical composition, soundness and setting time on the other hand were essential features of the first importance, and they had no alternatives. It was generally recognised that standard specification limits for strength, whether tensile or compression, could not approximate to the results obtained in practice because the specification limits were minimum limits only, and as the testing was not an exact science there must be a margin for the varying degree of skill and experience of the people who made such tests. The manufacturers would no doubt agree to an increase in the specification requirements if they could be sure that tests would be made only by competent people.

The author's calculations of cost were not very convincing. The price of cement packed and delivered in London included heavy overhead charges which were not reduced by variations in the nature of the cement. Manufacturing charges might actually be increased rather than reduced by making a variety of grades. Although the price of standard cement to-day had fallen to practically the pre-war level, the workers in the industry were receiving more than double the wages paid before the war, and the manufacturer had to pay higher fuel prices, taxes, and so on. That showed the advantage of being able to produce a standardised article on a big scale.

The author had advocated returning to the returnable jute bag, but in the speaker's view the freedom from trouble resulting from the use of the paper bag was not likely to be abandoned readily. It was quite practicable to pack different cements in distinctive paper bags; in fact, it was regularly done, and there was no confusion.

Mr. B. Hellstrom said the ageing of concrete in gravity dams was generally due to the action of frost, ice, temperature variation, and other atmospheric conditions, and secondly to the disintegrating effect of water percolating through the concrete. Deterioration due to percolating water was caused by the water dissolving calcium hydroxide in the cement. As the decomposition continued cohesion between the particles of the concrete gradually ceased, and the concrete was eventually changed into a soft mass of stone and sand mixed with what looked like a brown sticky glue and often containing organic matter. It was easy to show by an experiment why such deterioration could take place. If hydrated cement was pulverised and shaken with distilled water about 18 per cent. by weight of the cement was dissolved in water after about 100 shakings, each time with fresh water. However carefully concreting was carried out and even with rich concrete and suitable water content, it was difficult to avoid a certain amount of leakage. It would therefore be of great value to have a special

cement having a greater resistance to the action of water than ordinary Portland cement, i.e., a cement with less solubility in water. This was the first requirement of the " one-star " standard.

Another problem in the construction of structures where great masses of concrete were used, was the prevention of heat development by the cement during setting and hardening. The highest figure he had seen on record of maximum temperature measured in mass concrete was 144 deg. F., and the maximum temperature rise 70 deg. F. This heat development created a difference of temperature between the surfaces and the centre of the structure, with the result that the stresses created thereby became so great that cracks would occur. Cement specially prepared for dams had been in use in various countries for two or three years. In Norway a power scheme had recently been completed where blast furnace slag cement had been used. The power company decided to have a cement with a low solubility in water, and appealed to the cement makers to manufacture such a cement. The makers were not prepared to do so, and the power company erected its own grinding mill at the site where it ground cement from cement clinker and blast-furnace slag. The concrete looked excellent, and the power company was convinced that it had found means of avoiding deterioration, which in the water of that particular river was very bad. In Italy there was extensive use of natural pozzolana, which, when mixed with rich lime, produced hydraulic mortar. In his opinion the effect of coarser grinding was overrated, and he did not think it was possible that a cement which would have to fill the requirements already stated as to solubility in water and heat of hydration could be obtained simply by ordinary Portland cement less finely ground. From the point of view of heat generation, experience from the Boulder Dam had shown that it was possible to obtain a low-heat cement more finely ground than ordinary Portland cement. He believed that the addition of pozzolana was the crux of the matter, and it might be of interest to mention that in principle three different ways had so far been tried to obtain a cement suitable for large dams and mass concrete works. First, America and Sweden had met with success in producing a modified cement outside the definition of Portland cement. Second, in other countries, including Germany and Norway, the result of the addition to Portland cement of artificial pozzolana containing a limited amount of lime such as blastfurnace slag appeared to have been favourable. Third, mixing Portland cement and natural or artificial pozzolanas free from lime had been done successfully in Italy, India and elsewhere, which seemed to indicate a third line of suitable approach.

Mr. R. P. Mears, B.A., said he considered the stresses allowed with the grade of cement now classed as ordinary were high enough and there was no particular advantage in the higher stresses in tension and so on provided by rapid-hardening cement. It was interesting to note that the stresses allowed in the Code of Practice for the three grades of cement gave no premium to rapid hardening. The difference was clearly due to the amount of control exercised over mixing, placing, materials, and so on. He considered the tensile test was a very

valuable and useful one. One could proportion the water and learn to watch the cements and know what was happening to them.

An experience which served to emphasise the value of testing had occurred to him in 1918, when an enormous quantity of cement had become like rock. He happened to have the facility of a paint mill; it was never intended for cement, and it was full of flints. The cement was put through the flints, and it had come out to a certain fineness, or an uncertain fineness—it would not compare with the fineness of the cement originally—but the fact remained that for ordinary class work such as foundations or plastering or something of that sort not very important, it was quite good enough. He had also had the opportunity of making a good many tests on reground neat cement briquettes and had been fortunate in obtaining corresponding figures from a good many manufacturers. It was surprising to find that one could regrind briquettes and obtain subsequently test figures approaching half those obtained the first time, with perhaps a somewhat different proportion of water.

Mr. J. G. Kay said he did not doubt that manufacturers would agree to put up the tensile test considerably if they knew the material was going to be tested by experienced people.

Mr. J. Mathieson said he gathered that in asking for three qualities of cement the lecturer hoped the lower grade would possess various advantages over the others, such as cheapness of manufacture, resistance to percolation of water, low heat development, and so on. Other speakers had disposed of the hope that a coarser-ground ordinary cement would serve in all those cases. But the purpose in having three qualities would be to produce three concretes of different strengths. When varying the quality of the cement only, however, one left out of account the other components of the concrete—the water, the aggregates, and the method of manufacture. No doubt different grades of concrete were desired in many cases, but the proper way of varying the quality of the concrete was that recommended by the recently issued Code of Practice for Reinforced Concrete work, where no particular mention was made of the strength of various qualities of cement used, but the permissible stresses were determined by actual experiment on the concrete.

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The Presence of Silt and Clay in Sands Used in Cement Mortars.

By D. G. R. BONNELL. M.Sc., Ph.D. (of the Building Research Station).

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A study of the literature on the influence of silt and clay in the sand used as aggregate in cement mortars shows that investigators are not unanimous in their conclusions. Thus Grün,[1] Mörsch,[2] and Agatz[3] maintain that when the clay is attached firmly to the surface of the aggregate particle it is definitely injurious to the cement. Kathrein[4] on the other hand found that the tensile strength of concrete was slightly increased by the presence of clay in the aggregate, and several other investigators state that clay has no deleterious effect on concrete.

In view of the uncertainty it is customary to reject aggregate containing high percentages of clay or silt, and for this purpose a satisfactory method of determining the combined silt and clay fraction (referred to in the following as the clay fraction) is necessary.

Of the more exact methods the one generally employed is that given in Appendix IIIA of the Report of the Reinforced Concrete Structures Committee of the Building Research Board; it is the same as that adopted by the American Society for Testing Materials[5] in which the following procedure is adopted. A representative portion of the sand sufficient to yield approximately 500 grams of dried material is dried to constant weight at a temperature not exceeding 110 deg. The dried material is placed in a pan and sufficient water added to cover the sample. The contents of the pan are agitated vigorously for fifteen seconds and then allowed to settle for fifteen seconds, after which the water is poured off, care being taken not to pour off any sand. This operation is repeated until the wash water is clear. As a precaution the wash water is poured through a 200-mesh sieve and any material retained thereon returned to the washed sample. The washed sand is dried to a constant weight at a temperature not exceeding 110 deg. The percentage—of the orginal dry weight of sand—of clay present can be calculated from the loss in weight. When check determinations are desired, the wash water is evaporated to dryness and the residue weighed.

The application of this method for determining the total clay present has the following serious disadvantages. (*a*) Part of the clay may be present as a firmly adsorbed film over the surface of the aggregate and washing in the manner described would probably not remove this layer. Such an adherent film of clay may quite conceivably be the fraction most important in determining the bonding

[1] *Zentr. Bauw.*, 1924, 4.
[2] *Der Eisenbetonbau*, 6 Aufl., 1 Bd., 1 Hälfte, p. 30, 1923.
[3] *Die rationelle Bewirtschaftung des Betons*, p. 105, Berlin, 1927.
[4] *Zement*, 1931, 20, 679, 702, 724.
[5] A.S.T.M., designation D. 136—28.

of the cement to the aggregate. (*b*) The time consumed in washing the aggregate until the wash water is clear is very considerable. In a series of aggregates tested the number of washings necessary varied from sixty in some samples to 120 in others. This entailed about two hours' continuous washing and a complete determination takes three hours. Check determinations by evaporation of the large quantities of water are very tedious.

The removal of the adsorbed clay layer mentioned under (*a*) can to a great extent be carried out by peptising the clay with a deflocculant. In order to test the efficiency of such a method for removing the clay film experiments were carried out using (i) distilled water and (ii) a very dilute sodium oxalate solution (6 c.c. of 0·2*N*-oxalate solution per 100 c.c. of water). A comparison of the results showed that the amount of clay removed had been considerably increased by the deflocculant.

TABLE I.

Sand.	Percentage of clay as determined with (i) distilled water	(ii) sodium oxalate solution.
A	1·13	2·43
B	2·25	2·60

The difference in the values obtained by the two methods will depend on whether there is a large amount of clay present in the adsorbed state.

It is clear, therefore, that the American Society for Testing Materials method is not entirely satisfactory, the results obtained being usually too low. Furthermore it is very doubtful whether, even when using a deflocculant, the whole of the absorbed layer is removed during this treatment.

Since it is by no means certain that the effect on concrete of the clay fraction will be independent of the manner in which it is held by the aggregate, it was decided to investigate other methods of separation of the clay. At the same time the opportunity was taken to test, by measuring the tensile strength of cement mortars, the relative effects of clay exhibiting differences in its ease of removal from the aggregate.

Two methods were employed as follows: (I) A weighed quantity of sand was shaken in a horizontal shaker for 4 to 6 hours with a known volume of dilute sodium oxalate solution (6 c.c. of 0·2*N*-sodium oxalate per 100 c.c. of water). At the end of this time the liquid was poured into a wide sedimentation tube (1½ in. diameter) and analysed. (II) A known weight of sand was placed in a metal or glass mortar with a measured volume of the dilute sodium oxalate solution and rubbed with a very soft rubber pestle for about 30 minutes. The liquid was then transferred into the sedimentation tube and the clay concentration determined as in (I).

The apparatus (Fig. 1) used in the analysis is a modified form of Andreasen's pipette method[6]. It consists mainly of a pipette P (volume about 10 c.c.) which can be gradually and steadily raised or lowered by means of a mechanical arrange-

[6] *Kolloidchem. Beih.*, 1928, 27, 349.

ment. The volume of P plus the connecting bore of tap T is determined by filling the pipette and bore of T with water; any excess drawn into B can be removed through the outlet C. By running the water into a bottle and weighing, the weight and therefore the volume of water are obtained.

The procedure for a clay determination is as follows. The sedimentation tube S with the suspension is placed in position as shown. The pipette P, with T closed, is then lowered until the tip touches the surface of the liquid in S. The reading of the pointer R on the scale L is taken and the pipette then gently lowered 10 cm. By opening T and gentle evacuation at V, P is filled with the suspension, after which T is closed and P raised. The excess of liquid in B is

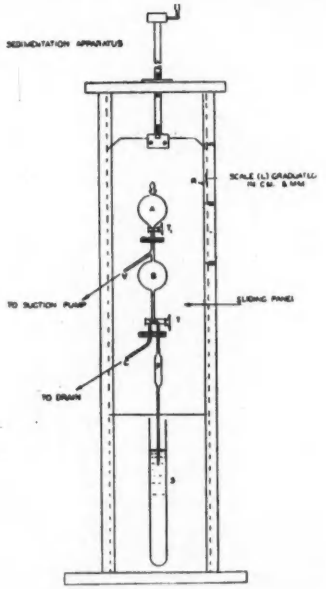


Fig. 1.

removed through C. The suspension is then run into a weighed crucible, any adherent suspension being washed down by water from A through T_1. The crucible is kept at 110 deg. until constant weight is attained and afterwards cooled and weighed. After correcting for the oxalate present the concentration of clay in the known volume is obtained and consequently the concentration of clay in the sand. By varying the time allowed for sedimentation before the determination is made, the concentration of various size particles can be determined.

For this investigation all particles smaller than 0·05 mm. or with a settling velocity more than 10 sec. per cm. have been included in the clay fraction. The time of settling allowed with the 10 cm. depth is therefore 100 seconds.

For less accurate work the apparatus may be substituted by an ordinary 10-c.c. pipette with a depth mark. The time allowed for settling can be changed to suit the depth at which the liquid is extracted from the sedimentation tube.

During the investigation of these two methods the sand: liquid ratio was kept at about 1 : 5 in order to maintain the concentration of the final suspension at a low value.

The results obtained with these two methods compared with those obtained with the A.S.T.M. method are given in Table II.

TABLE II

Sand	Percentage of clay as determined by method		
	A.S.T.M.	I	II
A	3·43	4·01	4·74
D	4·19	4·16	4·19
H	2·25	2·64	3·46
I	2·59	3·66	4·03

Examination of the table shows that the methods (I) and (II) yield higher results than the A.S.T.M. method. The values for (I) are lower than those for (II), probably due to insufficient shaking—a difficulty often encountered in soil analyses.

The pestle method (II) is more efficient and expeditious than the other methods. A complete determination can be finished in one hour, that is in about two hours less than by the A.S.T.M. method; furthermore, the difficulty of removing the absorbed layer of clay from the sand particle is overcome.

Comparative experiments with sodium carbonate and sodium oxalate showed that the former is quite as efficient as the latter for peptising the clay, as shown in Table III.

TABLE III

Sand	Percentage of clay after treatment with	
	sodium oxalate	sodium carbonate
F	5·50	5·31
G	6·26	6·17

Since, when used in cement mortars, the sand would come into contact with a practically saturated solution of lime, it was decided to determine whether lime could behave as a deflocculant. For this purpose determinations were carried out using saturated lime water. In a typical experiment the percentage of clay found with distilled water was 2·25, with sodium oxalate 2·60, and with lime water 1·47. It will be observed that the lime water behaves more like a coagulant than a deflocculant. This behaviour is of importance in cement-sand mortars because any clay adsorbed on the sand surface will not be removed during mixing, except in so far as the actual friction during this process may remove the clay film.

Effect of the Presence of Clay on the Tensile Strength of Cement Mortars.

The tensile strengths developed by cement-sand mortars at 1 and 7 days were determined with samples of the various sands after they had been submitted

to the following treatments: (*a*) In the naturally damp condition as received from the pit. (*b*) After the sand had been dried at 110 deg. (*c*) After washing by the A.S.T.M. method and then drying at 110 deg. (*d*) After cleaning by the pestle method with sodium oxalate solution (removing all traces of oxalate with distilled water) and drying at 110 deg.

The series of tests with each sand was carried out at the same consistency, the water content in the sand under test (*a*) being determined and taken into consideration. The results obtained are reproduced in Table IV. In this table the strength results are the mean of values obtained from three samples except in the cases marked * and † in which two and four samples respectively were tested. The differences which are shown, by the application of statistical tests, to be significant are given in heavy type.

TABLE IV.

Sand	% clay as received	I. Tensile strength as received		II. Decrease from I in tensile strength on drying sand at 110°		% clay after washing with A.S.T.M. method	III. Increase from I in tensile strength on washing sand by A.S.T.M. method		IV. Further increase in strength on washing with oxalate method	
		1 day, lb./sq. in.	7 days, lb./sq. in.	1 day, lb./sq. in.	7 days, lb./sq. in.		1 day, lb./sq. in.	7 days, lb./sq. in.	1 day, lb./sq. in.	7 days, lb./sq. in.
A*	4·74	420	635	—	—	1·3	119	100	47	136
E	4·89	496	700	10	−3	1·5	68	101	24	2
F	5·5	424	604	44	0	2·2	0	−7	0	7
G	6·26	403	624	4	12	0·95	54	91	12	60
H†	3·46	518	670	—	—	—	—	—	0	139
I†	4·03	500	785	13	134	—	—	—	80	150
J	6·58	386	586	16	11	1·51	112	128	49	55
K	2·07	466	684	10	22	0·8	45	123	6	3
L	7·13	397	649	—	—	0·10	43	81	28	68
M	0·76	425	624	—	—	0·76	—	—	53	125
N	0·23	436	696	—	—	0·23	—	—	58	64
O	0·03	511	687	—	—	0·03	—	—	11	42
P	3·7	383	611	50	55	0·87	12	−2	0	41
Q	4·18	471	697	3	−50	1·16	2	50	—	54
R	14·86	275	449	6	1	2·47	−40	24	2	0
S	13·46	261	393	−5	−61	0·96	116	341	10	30
T	33·6	251	429	35	−13	6·55	49	143	−25	39
U	1·67	396	639	−6	−120	0·97	53	136	2	43
V	4·56	454	731	—	—	2·02	21	30	73	91
W	2·78	389	723	—	—	1·08	−33	−16	3	20

Examination of the results for the twenty sands tested shows that the effect on the strength of the presence of clay in sands used in cement mortars cannot be well predicted by a simple clay analysis. In all these cases tested, with the exception of F, R, and W, there is a very marked increase in the strength of the mortars when made with clean or partly clean sand. It seems significant that of the three exceptions F and W are soft fine sands while R was a fine moulding sand.

This increase in strength is appreciable even in the 24-hour age and generally becomes more pronounced in the 7-day age. It does not appear to bear any relation to the quantity of clay originally present in the sand; e.g., sand P with 3·7 per cent. clay gives an increase of 80 lb. per square inch at 7-day age, sand E with 4·9 per cent. clay gives an increase of 101 lb. per square inch, whilst sand K with only 2·07 per cent. clay shows an increase of 130 lb. per square inch.

This means that within certain limits the quantity of clay gives no indication of the deteriorating effect on the strength of the mortars.

This is further emphasised when the strengths developed with sands treated with the A.S.T.M. and oxalate methods are compared. It is found that in a large number of cases there is a very appreciable increase in strength when the water-washed sand is further cleaned with the deflocculant even though the total quantity of clay removed is small; e.g., sand M with 0·76 per cent. clay gives 125 lb. per square inch and sand A with 1·30 per cent. clay gives 136 lb. per square inch in the 7-day age. From these results it appears that the effect of clay at moderate concentrations on the tensile strength depends on the form in which the clay is present in the sand. When the clay is present as nodules it would be expected that the deteriorating action on the strength of mortars made from the sand would be small, since the clay would be similar to a soft aggregate. The clay in this form might conceivably affect the weathering qualities of the mortar due to (*a*) the leaching out of the clay and (*b*) moisture movements of these particles in the mortar.

The clay fraction which produces the greatest effect is probably the fraction which is present as a film on the sand surface and fills the minute cracks in the sand particles. The adhesion of this clay film to the sand will depend on several factors such as the kind of clay, the dispersion of the clay, the state of the sand surface, etc. In some cases this film would be partly removed by washing with water alone whilst in other cases it could be separated from the sand only by means of a deflocculant. This was corroborated by microscopical examination, which showed that the sand grains treated only with water were much more contaminated with clay than were those treated with oxalate as in method (II). Even in the latter case the clay had not been completely removed from the minute cracks present in the sand particles.

The removal of this film would (*a*) affect the adhesion between the sand and cement due to the fact that the interfaces sand-clay-cement would be replaced by a sand-cement interface (this would probably increase the strength of the mortar); (*b*) by removing the clay from the cracks and crevasses in the sand grains, increase the area of sand-cement interface.

With regard to the decrease in strength due to the presence of clay, the figures in Table IV indicate that in sands containing up to about 7 per cent. of clay the reduction in strength is generally about 15 to 25 per cent. of the strength attained with the clean sand. For reductions of the order of 50 per cent. a high clay content, viz. of the order of 13 per cent., seems necessary.

In cases where strength only is important the A.S.T.M. method of silt and clay determination is probably sufficiently reliable to detect sands which give low strengths due to high clay content, although it takes no consideration of the clay fraction which is present as an adhering layer on the surface of the sand grains. Whether this latter fraction influences the other properties of mortars and concretes, as for example weathering and movements due to moisture sorption, can only be decided by further investigation.

Standard Methods of Testing Cement and Concrete Recommended by the New Code of Practice.

A new Code of Practice for Reinforced Concrete has been prepared by a committee formed at the request of the Ministry of Health and the London County Council to make recommendations on which new regulations for reinforced concrete might be based in the light of the developments which have taken place since the L.C.C. Regulations were revised many years ago. The recommendations contained in the new Code are not obligatory, but it is anticipated that they will be adopted as they stand or with revision by most local authorities responsible for the regulation of building. The Code recommends the following standard methods of testing concrete and concrete materials.

Test for Organic Impurities in Sands.—This method of test is an approximate method of determining the presence of injurious organic compounds in natural sands which are to be used in cement mortar or concrete. The principal value of the test is to furnish a warning that further tests of the sands are necessary before they are approved for use.

A representative test sample of sand, weighing about one pound, shall be obtained by quartering. A 12-oz. graduated clear glass bottle shall be filled to the 4½-oz. mark with the sand to be tested. A 3 per cent. solution of sodium hydroxide in water shall be added until the volume of the sand and liquid indicated after shaking is 7 liquid ounces. The bottle shall be stoppered, shaken vigorously and then allowed to stand for 24 hours. A standard colour solution may be prepared by adding 2.5 c.c. of a 2 per cent. solution of tannic acid in 10 per cent. alcohol to 97.5 c.c. of a 3 per cent. sodium hydroxide solution. This should then be placed in a 12 oz. bottle, stoppered, shaken vigorously, and allowed to stand for 24 hours. After standing 24 hours, the colour of the clear liquid above the sand shall be compared with the colour of the standard colour solution prepared at the same time and in accordance with the method described above, or with glass or other suitable standard of a colour similar to that of the standard solution.

Decantation Test for Sand and Other Fine Aggregates.—This method of test covers the determination of the total quantity of silt, loam, clay, etc., in sand and other fine aggregates. This determination of the percentage of silt, clay, loam, etc., will include all water-soluble material present, the percentage of which may be determined separately as desired.

The sample must contain sufficient moisture to prevent segregation and shall be thoroughly mixed. A representative portion of the sample sufficient to yield approximately 500 grams of dried material, shall then be dried to a constant weight at a temperature not exceeding 110 deg. C. (230 deg. F.). The dried material shall be placed in a pan of approximately 9in. (230 mm.) in diameter, and not less than 4in. (102 mm.) in depth, and sufficient water added to cover the sample (about 225 c.c.). The contents of the pan shall be agitated vigorously for 15 seconds and then be allowed to settle for 15 seconds, after which the water

shall be poured off, care being taken not to pour off any sand. This operation shall be repeated until the wash water is clear. As a precaution, the wash water shall be poured through a B.S. No. 200-mesh sieve and any material retained thereon returned to the washed sample. The washed sand shall be dried to a constant weight at a temperature not exceeding 110 deg. C. (230 deg. F.).

The results shall be calculated from the formula :

Percentage of silt, clay, loam, etc. =

$$\frac{\text{Original dry weight—weight after washing}}{\text{Original dry weight}} \times 100.$$

When check determinations are desired, the wash water shall be evaporated to dryness, the residue weighed and the percentage calculated from the formula :

Percentage of silt, loam, clay, etc. =

$$\frac{\text{Weight of residue}}{\text{Original dry weight}} \times 100.$$

Preliminary Decantation Test for Sand and Other Fine Aggregates.—This test is intended as a guide to the quantity of silt, loam, clay, etc., and where an aggregate passes the test it shall be deemed unnecessary to carry out the standard sieve analysis of aggregates described later.

A sample of the sand to be tested shall be placed in a 200 c.c. measuring cylinder filled to the 100 c.c. mark. Clean water shall be added up to the 150 c.c. mark. The mixture shall be shaken vigorously and the contents allowed to settle for one hour. The volume of silt visible at the surface of the sand shall be noted and recorded as the percentage volume of silt in the sand. The aggregate shall be deemed satisfactory when this percentage volume does not exceed 6 per cent.

Sieve Analysis of Aggregates.—A representative test sample of the aggregate as received on the works shall be selected by quartering. It shall weigh not less than (*a*) fine aggregate, 3 lb. ; (*b*) coarse aggregate, 10 lb. ; (*c*) where fine and coarse aggregates are to be used combined, 15 lb. The sample shall be dried to constant weight at a temperature not exceeding 110 deg. C. (230 deg. F.).

The sieves shall be of square-mesh wire cloth and shall be mounted on substantial frames constructed in a manner that will prevent loss of material during sieving. The size of wire and sieve openings shall conform to the B.S.S. for sieves. Unless otherwise stated the sample shall be separated into a series of sizes by means of the following sieves, 1½-in., ¾-in., ⅜-in., $\frac{5}{16}$-in., No. 7, No. 14, No. 15, No. 52, and No. 100. Sieving shall be continued until not more than 1 per cent. by weight of the residue passes any sieve during one minute. Each size shall be weighed on a balance or scale which is sensitive to 0.001 of the weight of the test sample. The percentage by weight of the total sample which is finer than each of the sieves shall be computed.

Consistency of Concrete.—This test is to be used both in the laboratory and during the progress of the work for determining the consistency of concrete. The test specimen shall be formed in a mould in the form of the frustrum of a cone with internal dimensions as follows : Bottom diameter, 8in. ; top diameter,

4in., and height, 12in. The bottom and the top shall be open, parallel to each other, and at right angles to the axis of the cone. The mould shall be provided with suitable foot pieces and handles. The internal surface shall be smooth. Care shall be taken to ensure that a representative sample is taken. The internal surface of the mould shall be thoroughly clean, dry and free from set cement before commencing the test.

The mould shall be placed on a smooth, flat, non-absorbent surface, and the operator shall hold the mould firmly in place, while it is being filled, by standing on the foot pieces. The mould shall be filled to about one-fourth of its height with the concrete which shall then be puddled, using 25 strokes of a $\frac{5}{8}$in. rod, 2ft. long, bullet pointed at the lower end. The filling shall be completed in successive layers similar to the first and the top struck off so that the mould is exactly filled. The mould shall then be removed by raising it vertically immediately after filling. The moulded concrete shall then be allowed to subside and the height of the specimen measured after coming to rest. The consistency shall be recorded in terms of inches of subsidence of the specimen during the test, which shall be known as the slump.

PRELIMINARY CUBE TESTS OF CONCRETE.—The method described applies to compression tests of concrete made in a laboratory where accurate control of materials and test conditions is possible.

The materials and the proportions used in making the preliminary tests shall be similar in all respects to those to be employed in the work. The water content shall be as nearly as practicable equal to that to be used in the work, but shall be not less than the sum of 30 per cent. by weight of the cement and 5 per cent. by weight of the aggregate unless specially authorised. For porous aggregates additional water shall be used to allow for the amount absorbed by the aggregates. Materials shall be brought to room temperature (58 to 64 deg. F.) before beginning the tests. The cement on arrival at the laboratory shall be mixed dry either by hand or in a suitable mixer in such a manner as to ensure as uniform a mixture as possible, care being taken to avoid intrusion of foreign matter. The cement shall then be stored in air-tight containers until required. Aggregates shall be in a dry condition when used in concrete tests. The quantities of cement, aggregate and water for each batch shall be determined by weight to an accuracy of 1 part in 1,000.

The concrete shall be mixed by hand or in a small batch mixer in such a manner as to avoid loss of water. The cement and fine aggregate shall first be mixed dry until the mixture is uniform in colour. The coarse aggregate shall then be added and mixed with the cement and sand. The water shall then be added and the whole mixed thoroughly for a period of not less than two minutes and until the resulting concrete is uniform in appearance. The consistency of each batch of concrete shall be measured immediately after mixing by the slump test made in accordance with the method of test for consistency already described. Providing that care is taken to ensure that no water is lost the material used for the slump tests may be re-mixed with the remainder of the mix before making the test specimen.

Compression tests of concrete shall be made on 6-in. cubes. The moulds shall be of steel or cast-iron with inner faces accurately machined in order that opposite sides of the specimens shall be plane and parallel. Each mould shall be provided with a baseplate having a plane surface and of such dimensions as to support the mould during filling without leakage and preferably attached by springs or screws to the mould. Before placing the concrete in the mould both the baseplate and the mould shall be oiled to prevent sticking of the concrete.

Concrete test cubes shall be moulded by placing the fresh concrete in the mould in three layers, each layer being rammed with a steel bar 15in. long and having a ramming face of 1in. square and a weight of 4 lb. For mixes of 1½in. slump or less, 35 strokes of the bar shall be given for each layer; for mixes of wetter consistency this number may be reduced to 25 strokes per layer. The test cubes shall be placed in moist air of at least 90 per cent. relative humidity and at a temperature of 58 deg. F. to 64 deg. F. for 24 hours ($\pm$ ½ hour) commencing immediately after moulding is completed. After 24 hours the test cubes shall be marked, removed from the moulds, and placed in water at a temperature of 58 deg. F. to 64 deg. F. until required for test.

Compression tests shall be made between smooth plane steel plates, without end packing, the rate of loading being kept approximately at 2,000 lb. per square inch per minute. One compression plate of the machine shall be provided with a ball seating in the form of a portion of a sphere, the centre of which falls at the central point of the face of the plate. Cubes shall be placed in the machine in such a manner that the load shall be applied to the sides of the cubes as cast.

For each age at which tests are required, three cubes shall be made and each of these shall be taken from a different batch of concrete. The acceptance limits are a difference of 15 per cent. of the average strength between the maximum and minimum recorded strengths of the three cubes. In cases where this is exceeded repeat tests shall be made excepting where the minimum strength test result does not fall below the strength specified.

Works Cube Tests of Concrete.—The method described applies to compression tests of concrete sampled during the progress of the work.

The test specimens shall be 6-in. cubes. The moulds shall be of steel or cast iron with inner faces accurately machined in order that opposite sides of the specimen shall be plane and parallel. Each mould shall be provided with a baseplate having a plane surface and of such dimensions as to support the mould during filling without leakage and preferably attached by springs or screws to the mould. Before placing the concrete in the mould both the baseplate and the mould shall be oiled to prevent sticking of the concrete.

Wherever practicable, concrete for the test cubes shall be taken immediately after it has been deposited in the work. Where this is impracticable samples shall be taken as the concrete is being delivered at the point of deposit, care being taken to obtain a representative sample. All the concrete for each sample shall be taken from one place. A sufficient number of samples, each large enough to make one test cube, shall be taken at different points so that the test cubes made from them will be representative of the concrete placed in that portion of the structure

selected for tests. The location from which each sample is taken shall be noted clearly for future reference. In securing samples the concrete shall be taken from the mass by a shovel or similar implement and placed in a large pail or other receptacle, for transporting to the place of moulding. Care shall be taken to see that each test cube represents the total mixture from a given place. Different samples shall not be mixed together but each sample shall make one cube. The receptacle containing the concrete shall be taken to the place where the cube is to be moulded as quickly as possible and the concrete shall be slightly re-mixed before placing in the mould.

The consistency of each sample of concrete shall be measured, immediately after re-mixing, by the slump test as already described. Providing that care is taken to ensure that no water is lost the material used for the slump tests may be re-mixed with the remainder of the mix before making the test cube.

The test cubes shall be moulded by placing the fresh concrete in the mould in three layers, each layer being rammed with a steel bar 15in. long and having a ramming face of 1in. square and a weight of 4 lb. For mixes of 1½in. slump or less, 35 strokes of the bar shall be given for each layer ; for mixes of wetter consistency the number may be reduced to 25 strokes per layer.

The cubes shall be stored at the site of construction, at a place free from vibration, under damp sacks for 24 hours ($\pm$ ½ hour) after which time they shall be removed from their moulds, marked and buried in damp sand until the time for sending to the testing laboratory. They shall then be well packed in damp sand or other suitable damp material and sent to the laboratory, where they shall be similarly stored until the date of test. Test cubes shall be kept on the site for as long as practicable but at least three-fourths of the period before test except for tests at ages less than seven days. The temperature of the place of storage on the site shall not be allowed to fall below 40 deg. F., nor shall the cubes be artificially heated. A record of the maximum and minimum day and night temperatures at the place of storage of the cubes shall be kept during the period the cubes remain on the site.

All compression tests shall be made between smooth plane steel plates without end packing, the rate of loading being kept approximately at 2,000 lb. per square inch per minute. One compression plate of the machine shall be provided with a ball seating in the form of a portion of a sphere, the centre of which falls at the central point of the face of the plate. All cubes shall be placed in the machine in such a manner that the load shall be applied to the sides of the cubes as cast.

The new Code is published in its entirety in a volume entitled " Explanatory Handbook on the Code of Practice for Reinforced Concrete," by W. L. Scott, M.Inst.C.E., Chief Engineer of Considère Constructions, Ltd., and W. H. Glanville, D.Sc., of the Building Research Station, and published by Concrete Publications, Ltd., price 8s. 6d. by post. The authors, who were actively engaged in the preparation of the new Code, give explanations and comments where necessary on its clauses, so that the meaning and intentions of the document are made clear.

The Chemical Constitution of Portland Cement Clinker.—III.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

(*Continued.*)

Researches of Rankin and Wright.—A great impetus to research on Portland cement clinker constitution was given in America by exhaustive studies of the various systems of calcium oxide with other components. Deductions as to the nature of clinker were made by employing the phase rule which applies to the equilibrium conditions of a heterogeneous system. Rankin and Wright[35] pointed out that calcium oxide, silica, and alumina constitute 90 per cent. of the whole of a normal Portland cement clinker. Hence studies of the systems calcium oxide-silica, calcium oxide-alumina, calcium oxide-alumina-silica, and alumina-silica would be of significance. Portland cement clinker is concerned only with a small portion of the system calcium oxide-alumina-silica. The experimental work for two component systems was as follows. Mixtures of the two components were heated in a platinum resistance furnace to a given temperature for a period sufficiently long to allow equilibrium to be attained as described above. When this condition was reached the product would contain only two compounds unless the exact composition of a compound had been used. The melt was quenched in mercury, with the result that any material which was liquid in the furnace would usually be a glass on quenching, whilst the crystalline material remained unchanged. If two crystalline phases were found together at equilibrium in a given composition the percentage of the ingredients was changed in succeeding heatings in one direction until, at a rigidly fixed ratio, there was found to be only one phase. The composition was known, so the optical properties of the compound were then accurately determined. The compound could then be identified when present in any mixture by noting the optical properties. In this way the three two-component systems were studied and the compounds possible under the conditions applied were prepared and identified. In the study of the three-component system calcium oxide-alumina-silica, a thousand different compositions and seven thousand heat treatments and microscopical examinations were made. Binary compounds, when they occurred, were identified from the previous work on the two-component systems and new compounds were detected as before by varying the composition until only one phase was present. It was then possible to represent the ternary system calcium oxide-alumina-silica by a two-dimensional triangular diagram drawn to scale. In this triangle we have (1) Pure components CaO, Al_2O_3 and SiO_2 represented at the apices of the triangle. (2) The binary compounds represented by points on the sides of the triangle. (3) The ternary compounds represented by points within the triangle. (4) Each point is definitely fixed by its composition, expressed as percentage by weight. (5) The final product of crystallisation of any mixture in the ternary system will consist of three solid

phases, except (*a*) when the composition is exactly that of a ternary compound, in which case only the one crystalline phase will be present, or (*b*) when the composition lies on the line separating two fields, in which case there will be two compounds present. (6) The large triangle is thus divided into a number of small triangles each representing a field in which the three compounds represented at the apices of these triangles occur. On passing from one of these triangles to an adjacent triangle, one compound disappears and a new one appears.

In the case of tricalcium silicate the compound was not at first observed in the study of the binary system because it dissociates into dicalcium silicate and calcium oxide without melting and does not occur as a primary phase in that system. In the ternary system there is a narrow field of stability for this silicate. Tricalcium aluminate is also unstable at its melting point when it dissociates, yielding calcium oxide and $5CaO.3Al_2O_3$. Rankin and Wright thus found that in the ternary system there is a field represented by the triangle whose apices denote the three compounds, tricalcium silicate, dicalcium silicate, and tricalcium aluminate. Hence in this field only these three compounds occur at equilibrium. They found, moreover, that the field represents the range of compositions for Portland cements, exclusive of minor constituents, according to analyses of cements from several sources. At equilibrium, therefore, only tricalcium silicate, dicalcium silicate, and tricalcium aluminate will be present in a cement prepared from the three components, lime, silica, and alumina in the proportion in which they are found in Portland cement. If equilibrium were not attained, as may happen in commercial cement, the adjacent compounds calcium oxide and $5CaO.3Al_2O_3$ would probably be the only additional compounds to be expected.

Although the system $CaO\text{-}Al_2O_3\text{-}SiO_2$ may be the most important in Portland cements, a complete understanding of the constitution and behaviour of commercial cement cannot be available until the compounds developed in other systems, which include such components as Fe_2O_3, MgO, have been worked out.

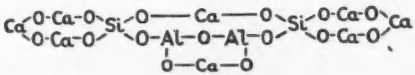
The American work has been discredited by several people, in particular by von Glasenapp and Kühl[36] The two chief objections raised are (1) Cement clinker is not the result of a process of fusion, but of sintering, a fact which precludes the application of the laws of equilibrium in heterogeneous systems; (2) ferric oxide plays a very important part in the production of clinker and is thus capable of profoundly modifying these conclusions.

Brownmiller and Bogue,[37] on the other hand, considered that the method of manufacture of Portland cement leads to the belief that a condition approaching equilibrium is attained in commercial clinker. A failure completely to reach equilibrium, however, may result in the presence of some free calcium oxide and a change in the relative proportions of the other compounds, but rarely in the elimination of one of these compounds with the formation of a different compound.

Gillson and Warren[38] studied several brands of clinker by the petrographic method and concluded that the two major constituents of Portland cement

clinker are both calcium alumino silicates, and that tricalcium and dicalcium silicates do not exist in Portland cement clinker. These conclusions arose chiefly from the following points: (*a*) There are certain discrepancies in indices of refraction of one of the components as compared with the refractive index of pure tricalcium silicate as prepared by Rankin and Wright; (*b*) the optic angle of the other component in the clinker was 20 deg. as contrasted with a "large" optic angle determined by Rankin and Wright for pure β-$2CaO.SiO_2$; (*c*) the analyses of separated fractions proves them to contain lime, silica, and alumina.

Janeckite.—Janecke[39] did not consider that tricalcium silicate exists. He stated that the existence of a real binary compound which can be identified only in a ternary system is altogether improbable. He investigated that part of the system CaO-Al_2O_3-SiO_2 which corresponded to average Portland cement clinker compositions and claimed to have established the existence of a new ternary compound of the formula $8CaO.Al_2O_3.2SiO_2$, which has been called Janeckite. This he made by melting the correctly proportioned raw mixture in an iridium crucible, with a removable bottom and separable sides, by means of a oxy-hydrogen blowpipe. It was then pulverised, returned to the crucible with a thermocouple inserted in it, and heated to 1,650 to 1,700 deg. C. in an electric furnace composed of two magnesia cylinders with retort carbon as a resistor. The cooling curve was then taken and a definite melting point found to be 1,382 deg. C. Janecke considered that such a solidification point can only occur for compounds or eutectic mixtures, and ruled out the latter since mixtures adjacent to $8CaO.Al_2O_3.2SiO_2$ solidify at lower temperatures. This uniform solidification, he stated, is not in agreement with the work of Rankin and Wright, according to which $8CaO.Al_2O_3.2SiO_2$ is a mixture. The structural formula he gave as



Thin section shows columnar crystals and irregular masses, optically positive, double refracting, extinguishing parallel or nearly parallel, and polarising in colours of the first order. The refractive index is greater than 1.54, that is, greater than Canada balsam. It should be noted that the optical properties given by Janecke are not sufficiently clearly stated to admit of the identification of Janeckite as either the orthosilicate or tricalcium silicate of Rankin and Wright.

Janecke stressed the point that Alite contains some alumina and that therefore it must be a ternary compound. He claimed that Alite is essentially $8CaO.Al_2O_3.2SiO_2$ and that clinker of average composition was made up as follows:

	Per cent.
$8CaO.Al_2O_3.2SiO_2$ (Alite)	47.15
$2CaO.SiO_2$ (Belite)	39.70
$3CaO.Fe_2O_3$ (Celite)	5.75
CaO (Felite)	7.40
	100.00

According to the majority of workers tricalcium ferrite does not exist under any conditions.

Rankin and Wright[40] disagreed with Janecke's conclusions and stated that tricalcium silicate does occur in the binary system $CaO\text{-}SiO_2$, although not as a primary phase in that system. They also showed experimentally that a mixture of the composition $8CaO + Al_2O_3 + 2SiO_2$ does not melt at 1,382 deg. C., and even at 1,600 deg. C. is only partially liquid. They also observed the heating and cooling curves of this mixture over the range 1,200 to 1,600 deg. C. The heating curve showed two breaks, one at 1,404 deg. C. and the other at 1,454 deg. C. On the cooling curve one break only was found at approximately 1,370 deg. C. The reasons for these breaks were established by making a series of quenches of the same composition. In these experiments the phases present were found to be :

At 1,391 deg. C. .. $3CaO.SiO_2$; $2CaO.SiO_2$; $3CaO.Al_2O_3$.
At 1,432 deg. C. .. $3CaO.SiO_2$; $2CaO.SiO_2$; glass.
At 1,475 deg. C. .. $3CaO.SiO_2$; glass.

It appeared therefore that (*a*) the break in the heating curve at 1,404 deg. C. is the temperature at which tricalcium aluminate goes into the liquid phase ; (*b*) at a temperature between 1,432 deg. C. and 1,475 deg. C. a break should result due to the solution of the dicalcium silicate. The cooling curve shows only one break, which is below the temperature 1,404 deg. C. because of undercooling which is common in silicate charges. Hence Rankin and Wright concluded that Janeckite is a mixture of tricalcium silicate, dicalcium silicate, and tricalcium aluminate, and that the break in the cooling curve is due to the solidification of the undercooled tricalcium aluminate, perhaps with dicalcium silicate.

Janecke[41] discounted the work of Rankin and Wright. He pointed out that these workers made observations on material heated for a comparatively short time to the desired temperature and then quenched in mercury, a process which does not favour crystal formation. Janecke took the cooling curve on material which had been heated to a much higher temperature and cooled the melt slowly, thus favouring crystal growth.

Wetzel[42] heated mixtures of pure calcium carbonate, alumina, and silica, the composition of which were identical with or near to that of Janeckite. Cooling curves were made and sections of the clinker were polished, etched with hydrofluoric or hydrochloric acid, and examined microscopically. His conclusions were that (*a*) only at high temperatures (1,670 deg. C. and over) can the crystals typical of Janeckite be obtained ; (*b*) these crystals increase in quantity with rise in temperature up to 1,800 deg. C. ; (*c*) it was impossible to produce these crystals unassociated with the usual forms of di- and tricalcium silicates ; (*d*) Janeckite is therefore not a compound but only a primary phase separating out of the glass.

Dyckerhoff[43] also obtained the crystalline phase known as Janeckite by fusion of the correct mixture in an oxy-hydrogen flame and holding it at 1,200 deg. C. for seventy hours. The phase separated consisted of fine needle-like aggregates with optical constants so close to those of tricalcium silicate that

differentiation by optical methods became difficult, the somewhat lower refractive index of Janeckite serving as the only means of doing so. A specific gravity determination gave a value of 3.090 whereas the calculated mean density of the three compounds tricalcium silicate, dicalcium silicate, and tricalcium aluminate was 3.190.

Hansen, Dyckerhoff, Ashton and Bogue[44] confirmed the separation of fibre-like aggregates from a mixture of the composition $8CaO + Al_2O_3 + 2SiO_2$ by heating to very high temperatures and allowing to cool slowly. They considered that if these aggregates are tricalcium silicate (as optical similarity indicates) then, from the equilibrium diagram of the system $CaO\text{-}Al_2O_3\text{-}SiO_2$ as prepared by Rankin and Wright, it followed that dicalcium silicate and tricalcium silicate would appear if the preparations were treated in such a way as to bring about equilibrium. A charge of powdered fused drops was heated at 1,600 deg. C. for three hours, cooled to 1,450 deg. C. during one hour and held at 1,400 to 1,450 deg. C. for thirty hours. The charge was at equilibrium after this period since a thin section was found to be made up of a uniform mixture of tricalcium silicate, dicalcium silicate, and tricalcium aluminate. The refractive indices of these compounds were measured by the immersion method to verify the observations made upon the thin section. These experiments demonstrate clearly that these preparations are composed at equilibrium of the three compounds, tricalcium silicate, dicalcium silicate, and tricalcium aluminate, instead of one ternary compound.

The possibility remained, however, that a ternary compound or solid solutions might exist in this region of the ternary system at high temperatures and decompose at lower temperatures giving, at equilibrium, these compounds. If this were the case X-ray studies might reveal the presence of such new phases. The X-ray data were obtained using the powder method. A mechanical mixture of the three compounds, tricalcium silicate, β-dicalcium silicate, and tricalcium aluminate was made in equimolecular proportions which results in the composition $8CaO + Al_2O_3 + 2SiO_2$. The X-ray spectrum of this mixture was identical with that of Dyckerhoff's fused drops with the exception of a few lines due to calcium oxide in the latter. Since all lines in the spectrum of the fused preparation corresponded to the lines in the spectrum of the four compounds, and no displacement of any of the lines or any appreciable change in the relative intensities could be detected, it seemed to follow that no compounds other than those four are present and that no solid solution is present. The fibrous aggregates therefore appear to be one of these four compounds, and their optical properties indicate that they consist of tricalcium silicate.

The form in which the tricalcium silicate crystallises from the drops seems to be dependent upon the conditions under which it is produced. In order to ascertain if it would be formed in the same way in other systems the composition $8CaO. + Fe_2O_3 + 2SiO_2$ was made up and drops prepared in the oxy-hydrogen flame. The same fibre-like crystals were obtained in this system. The birefraction and mean refractive index also indicated that they were tricalcium

silicate. This constitutes further proof that the formation of fibrous aggregates is not dependent upon alumina, and that therefore the aggregates are not a ternary compound or a solid solution of CaO, Al_2O_3 and SiO_2.

Janecke[45] refuted these findings, claiming that they were based upon the examination of the decomposition products of the compound $8CaO.Al_2O_3.2SiO_2$. He prepared X-ray spectra of the compound and concluded that the X-ray spectrum of Janeckite was identical with that of dicalcium silicate. He concluded that Janeckite and dicalcium silicate were isomeric.

Kühl[46] prepared a mixture of the composition $8CaO + Al_2O_3 + 2SiO_2$ from pure materials, very small amounts of Fe_2O_3 and MgO being present, and burned it for one and a half hours in a laboratory shaft kiln at 1,450 deg. C. The sintering range was very narrow, some pieces being underburned and others fused, though the furnace temperature was very uniform. Hence Kühl supposed that a single compound with a sharp melting point was present. Thin sections of properly sintered specimens showed a uniform structure, but the crystals were so small that they were difficult to examine ; they were weakly, doubly refracting and seemed to show parallel extinction. Sections were submitted to Janecke who said they corresponded with the preparations of Janeckite but that the crystals were smaller. Kühl therefore concluded that a compound of the composition $8CaO.Al_2O_3.2SiO_2$ existed. The evidence presented does not justify this conclusion, for the melting point was not checked either by heating or cooling curves, nor is there proof that the crystals are one entity of the chemical formula $8CaO.Al_2O_3.2SiO_2$.

Janecke[45] claimed that Alite is essentially Janeckite, $8CaO.Al_2O_3.2SiO_2$. From its low specific gravity, the low strength and rapid setting, Kühl,[36] however, concluded that this substance is not Alite. He emphasised the fact that the formula of Janeckite requires 102 parts by weight of alumina to 120 of silica. Such a compound could never constitute the Alite of clinker, since there is copious Alite formation in clinkers which are very low in alumina ; Alite of the composition of Janeckite present in a clinker of low alumina content would only constitute a minute fraction of the whole mass. Janecke,[45] as the result of X-ray investigations, has abandoned this conception and now considers that Alite is an isomorphous mixture of Janeckite and dicalcium silicate. As, however, it is now well known that really good quality clinker contains no appreciable amount of free calcium oxide, Kühl pointed out that Janecke's new view was untenable. If it were tenable the Alite of a high-limed clinker low in alumina would consist essentially of dicalcium silicate, and such a clinker would contain an appreciable amount of free lime.

Nagai and Naito[47] heated a raw mix of the composition $8CaO+Al_2O_3+2SiO_2$ and obtained a sound and satisfactory product. This does not, of course, postulate the existence of a compound of the formula of Janeckite.

Brownmiller and Bogue,[48] using X-ray methods, stated that the existence of the compound $8CaO.Al_2O_3.2SiO_2$ cannot be authenticated either in the system

CaO-Al_2O_3-SiO_2 or in Portland cements. On burning a mixture of this composition, $3CaO.SiO_2$, β-$2CaO.SiO_2$ and $3CaO.Al_2O_3$ are formed, together with free CaO when equilibrium is incomplete.

(To be continued.)

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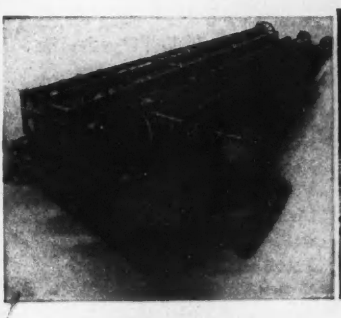

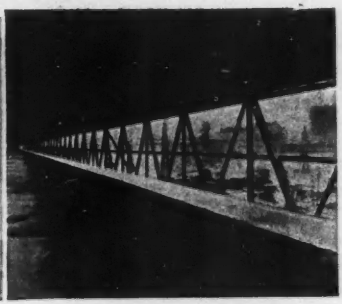

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